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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>D06M 14/00, 14/02, 14/08, 14/16, 23/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/13024</b> <b>(43) International Publication Date:</b> 10 April 1997 (10.04.97)
<b>(21) International Application Number:</b> PCT/GB96/02220 <b>(22) International Filing Date:</b> 9 September 1996 (09.09.96)  <b>(30) Priority Data:</b> 9519824.8 29 September 1995 (29.09.95) GB  <b>(71) Applicant (for all designated States except US):</b> THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, DRA Farnborough, Hampshire GU14 6TD (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> WILLIS, Colin, Robert [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). BREWER, Stuart, Anson [GB/GB]; CBDE, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB).  <b>(74) Agent:</b> SKELTON, Stephen, Richard; D/IPR (DERA) Formalities, Poplar 2, MOD (PE) Abbey Wood #19, P.O. Box 702, Bristol BS12 7DU (GB).		<b>(81) Designated States:</b> GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> FIBRE REACTIVE POLYMERS  <b>(57) Abstract</b>  A group of polymers for treatment of cellulose based materials which are characterised by a functional group which binds the polymer to the material. This allows treatment of, for example cotton based fabrics, to improve, for example, their oil and water repellent properties.		

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FIBRE REACTIVE POLYMERS.

The present invention relates to a group of polymers suitable for binding to cellulose or woollen based material and is useful for the treatment of cloth, linen fabric and the like.

The durability of certain functional treatments (e.g. water or oil repellency) on cellulose based fabrics can be improved by the addition of cross-linkable resins to their formulations. Depending on the type of resin employed, fixation to the cloth may occur under acidic conditions (eg with dimethyloldihydroxyethylene urea) or under neutral conditions (eg with a blocked polyisocyanate).

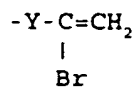
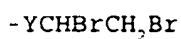
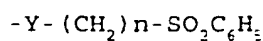
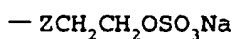
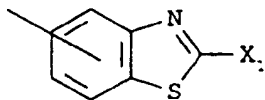
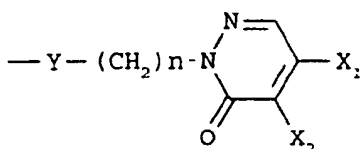
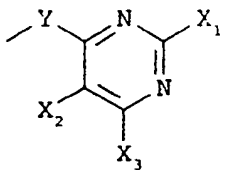
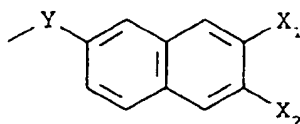
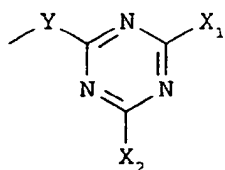
The use of certain groups, for example triazines, to bind molecules to cellulose based, and other, materials is known from the chemistry of reactive dyes. For example, the 2,4-dichloro-6-aminotriazyl group is used to bind a family of dyes, known commercially as Procion dyes, to cellulose materials (see for example, The Chemistry of Synthetic Dyes, Vol. IV - Reactive Dyes, K Venkataraman Ed., Academic Press.).

The use of fluoroalkyl compounds to improve the oil and water repellency of articles is described, for example, in GB 1,102,903. These compounds are non-polymeric and the invention described therein requires the use of organic solvents whereas the current invention may be carried out in aqueous solvents.

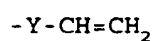
Whilst resin treatments can improve the durability of certain finishes and impart dimensional stability and durable press properties to fabrics, the acid catalysts required to bring about the cross-linking reactions can damage acid sensitive cloth such as cotton. Moreover, excessive cross-linking can also lead to a reduction in abrasion resistance (see for example Textile Chemist and Colorist, 1995, Vol. 27, page 17, R J Harper and Melliand Textilber., 1986, Vol. 67, p.E61-5, J. Hearle). Problems also arise with resins that contain formaldehyde and this has prompted considerable research into the development of cross linking agents that do not contain this compound (see for example Textile Res. J., 1994, Vol.64, page247, N. R. Bertoniere et al).

According to this invention, a polymer for the treatment of materials is characterised by a plurality of side groups of general formula -A-Az, where:

A = (CH<sub>2</sub>)<sub>n</sub>, wherein non adjacent CH<sub>2</sub> groups may be replaced by O, CO<sub>2</sub>, OCO  
OCO<sub>2</sub>, or phenylene and n may have any integral value from 0 to 16,  
and Az is selected from:



and



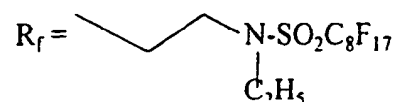
where  $X_1, X_2$  etc are independently selected from halogen, -NHR, -SO<sub>2</sub>CH<sub>3</sub>, Alkyl, Aryl, -O-Alkyl or -O-Aryl and at least one of  $X_1, X_2$  etc per group Az is halogen:

$Y = -NH-, -NR- (R=Alkyl), -NHCO-, -O-,$  or  $-S-$  and

$Z = -SO_2NH-$  or  $-SO_2-$

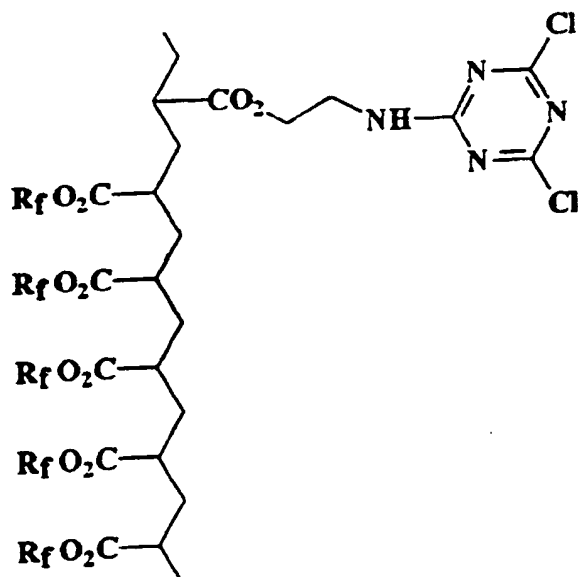
In a preferred embodiment, the polymer also contains fluorine bearing side groups.

In a further preferred embodiment, the polymer also contains side groups bearing  $R_f$  where:



In a further preferred embodiment, the polymer contains the side group -CO<sub>2</sub>R<sub>f</sub>.

In a further preferred embodiment the polymer has the repeat unit:



According to a second aspect of the invention, a material is provided with improved physical properties by virtue of treatment of said material with the polymer of the first aspect of the invention.

According to a third aspect of the invention, a method is provided of treating a material with the polymer of the first aspect of the invention. Preferably the material is treated in an aqueous solution.

Durability of the polymers may be further improved by the addition of polyhydric alcohols.

The invention will now be described, by way of non-limiting example, with reference to figures 1 which shows the reaction scheme during the production of a polymer used in a particular embodiment of the invention. Although the following example relates to the treatment of fabrics to improve their oil and water repellent properties, this should not be seen as limiting. The invention may be used in other situations where treatment of material with a polymer may improve physical properties eg. abrasion resistance or fire retardance.

## **EXPERIMENTAL**

Referring to figure 1, a solution of 1250 parts surfactant FC 126 (available from Fluorochem Ltd.) in 60000 parts distilled water was added to a stirred solution containing 1050 parts 2,4-dichloro-6-(N-(2-acrylyl)ethylamino)-s-triazine 1, 22500 parts 2-(N-ethylperfluorooctylsulphonamide)ethyl acrylate 2, and 125 parts octanethiol ( $C_8H_{17}SH$ ) in acetone. The mixture was deaerated with argon and then warmed to 55°C before addition of 125 parts potassium persulphate. The temperature was increased to 65°C and stirring maintained under a blanket of argon for 20 hours. The resulting dispersion of polymer 3 was allowed to cool, filtered and stored (total solids content = 20%).

**Treatment of Cotton Fabrics using Formulation of Polymer 3.**

**Sample A:** The formulation of polymer 3 obtained from the above experimental procedure was diluted to 30g/litre with a 7.5% w/v sodium carbonate solution. The cotton fabric was immersed in this solution, pad mangled to a 150% wet pick-up, and cured at 150°C for 10 minutes.

**Sample B:** Cotton fabric was treated in an identical manner to that described for sample A, except that the polymer formulation was diluted with distilled water rather than sodium carbonate solution.

Prior to repellency tests and laundering, the cloth samples were washed with detergent (Tepol, TM) and rinsed with water. Repellency rating are in accordance with AATCC Test Method 118 - 1978, (see AATCC Technical Manual 55, p242 (1979)).

Tables 1 and 2 show the results of oil (O) and water (W) repellency tests carried out on samples A and B.

**Table 1.**

	Sample A	Sample B
Initial	O5 W5	O5 W5
5hr Soxhlet with trichloroethylene	O5 W5	O2 W4
3hr Soxhlet with benzotrifluoride	O4 W4	O3 W3

**Table 2.**

	Sample A	Sample B
Initial	O5 W5	O5 W5
10min boil	O5 W5	O2 W3
10min boil	O5 W5	W
20min boil	O4 W4	W
45min boil	O4 W4	

Tables 1 and 2 show that a more durable oil and water repellent finish results when base is included in the formulation. This is consistent with reaction between cellulosate anions in the cotton (formed by reaction of hydroxyl groups with the base) and the fibre reactive groupings on the polymer.

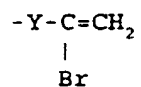
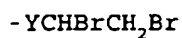
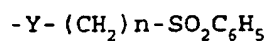
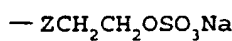
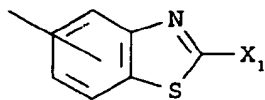
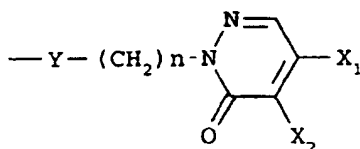
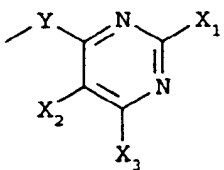
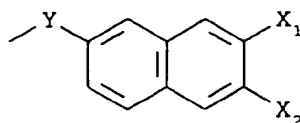
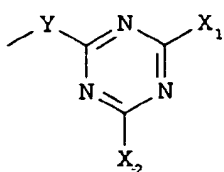


Claims

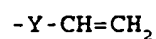
1. A polymer for the treatment of materials, characterised by a plurality of side groups of general formula -A-Az, where:

A = (CH<sub>2</sub>)<sub>n</sub>, wherein non adjacent CH<sub>2</sub> groups may be replaced by O, CO<sub>2</sub>, OCO, OCO<sub>2</sub>, or phenylene and n may have any integral value from 0 to 16;

and Az is selected from:



and



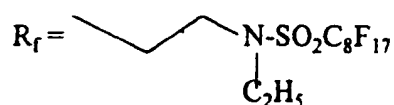
where  $X_1, X_2$  etc are independently selected from halogen, -NHR, -SO<sub>2</sub>CH<sub>3</sub>, Alkyl, Aryl, -O-Alkyl or -O-Aryl and at least one of  $X_1, X_2$  etc per group Az is halogen;

$Y = -NH-, -NR- (R=Alkyl), -NHCO-, -O-,$  or  $-S-$  and

$Z = -SO_2NH-$  or  $-SO_2-$

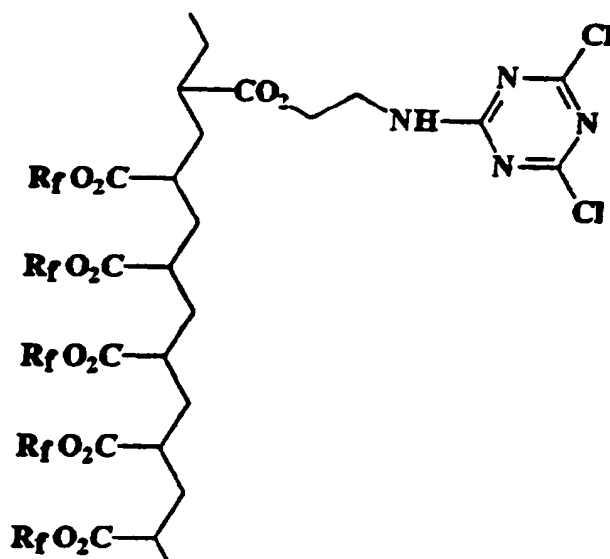
2. The polymer of claim 1 and further containing fluorine bearing side groups.

3. The polymer of claim 2, containing side groups bearing  $R_f$  where:



4. The polymer of claim 3, containing the side group -CO<sub>2</sub> $R_f$ .

5. The polymer of claim 4 having the repeat unit:

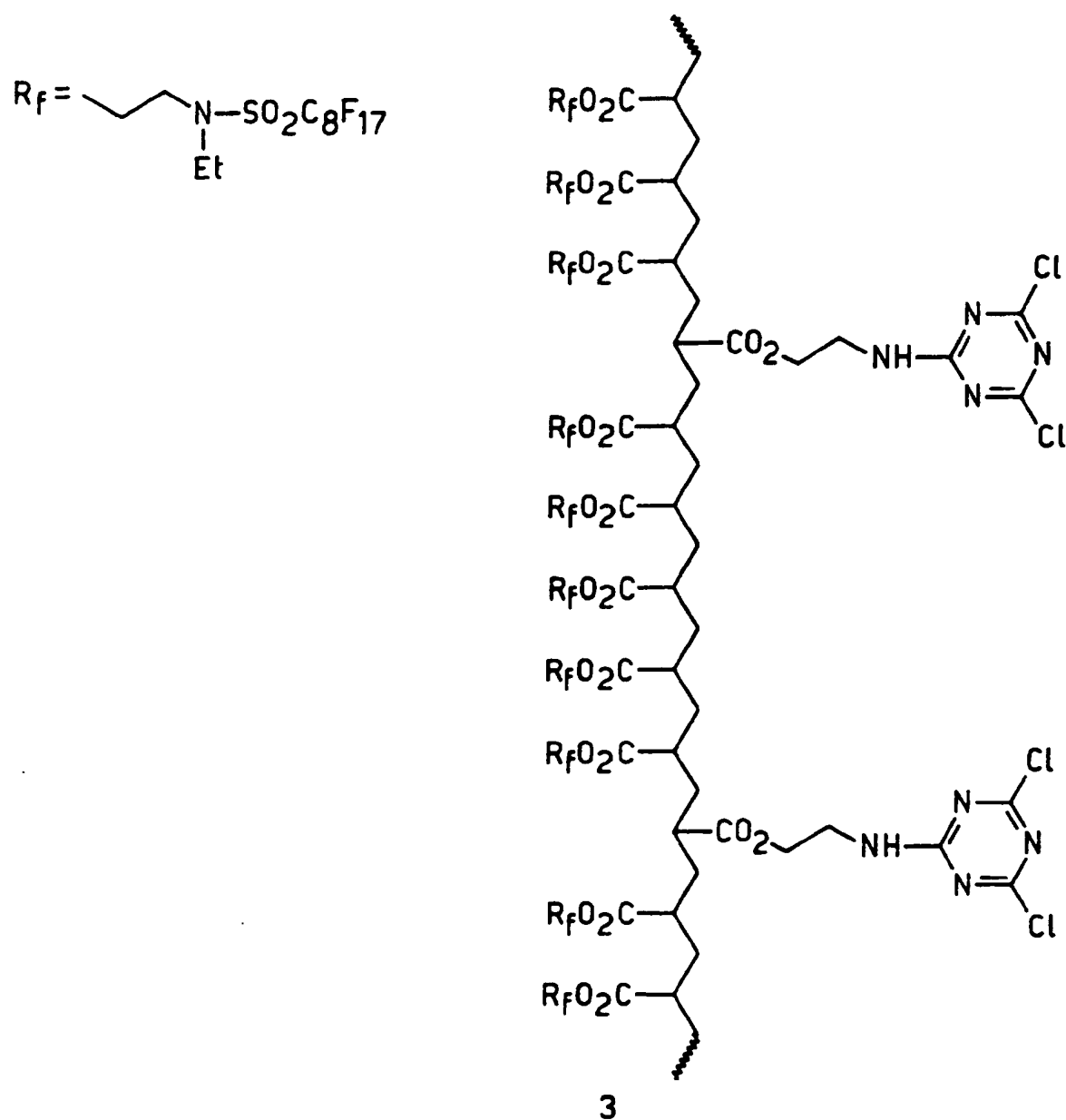
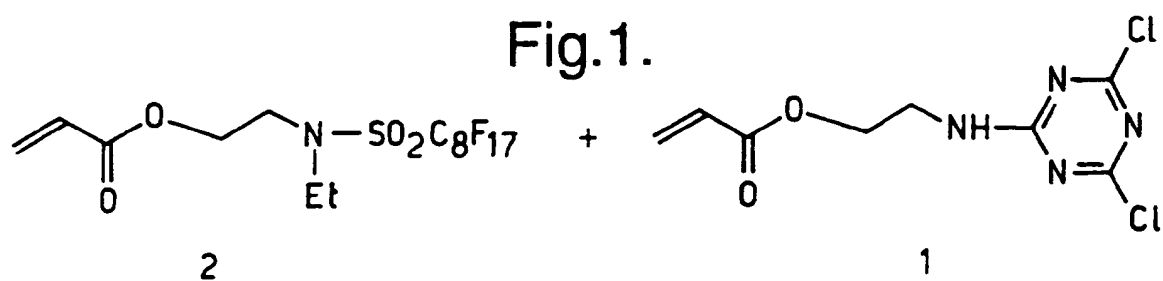


6. A material characterised by treatment with a polymer as described in claim 1.

7. A method of treating a material characterised by the use of an aqueous formulation of the polymer described in claim 1.

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Fig.1.



# INTERNATIONAL SEARCH REPORT

Intern al Application No  
PCT/GB 96/02220

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 D06M14/00 D06M14/02 D06M14/08 D06M14/16 D06M23/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D06M B05D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, Y	GB 2 291 439 A (SECR DEFENCE) 24 January 1996 see the whole document ---	1-7
Y	US 4 507 324 A (OLIVE SALVADOR ET AL) 26 March 1985 see the whole document ---	1-7
Y	WO 92 18332 A (PEACH STATE LABS INC) 29 October 1992 see the whole document ---	1-7
A	US 4 032 495 A (PERRONIN JEAN ET AL) 28 June 1977 see the whole document ---	1-7
A	EP 0 221 046 A (MONSANTO CO) 6 May 1987 ---	
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

14 February 1997

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International Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 95 24976 A (DOW CHEMICAL CO) 21 September 1995</p> <p>-----</p>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/02220

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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